

NATURE AND STRUCTURE OF CALCIUM SPECIES DISPERSED ON CARBON: XANES AND EXAFS STUDY

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INTRODUCTION

In a previous publication (1) the thermal behavior of calcium-carbon samples with different metal contents has been analyzed by temperature programmed desorption (TPD). The main purpose of that study was to investigate the nature and structure of calcium species dispersed on the carbon.

The most relevant aspects deduced from such study can be summarized as follow: 1) All the proton from carboxylic groups, present in the carbon surface, are ion-exchanged by Ca^{2+} ions with a 2/1 stoichiometry. 2) For calcium contents lower than the saturation of available carboxylic groups on the carbon, the ion-exchanged calcium has its coordination sphere completed with H_2O and CO_2 molecules with a coordination number of six, indicative of having an atomic distribution through the carbon matrix. 3) For high levels of calcium loading, exceeding the saturation, the ion-exchanged calcium acts as a nucleation site where crystals of calcium acetate (precursor used) grow.

TPD is not a technique which provides direct information on the structure of the analyzed species, therefore, a complementary study with an spectroscopic technique able to supply such information will be very convenient to confirm the conclusions above mentioned.

X-ray absorption fine structure spectroscopy (XAFS) has gained a great utility in the field of catalysis due to the specific information which can be obtained concerning local structure and bonds of the element examined (2-10). This technique gives information on atomic distances, coordination number and disorder degree from the interaction of the emitted electrons with the atomic environment of the absorbing atom (EXAFS) as well as information about the electronic structure and the symmetry of the atom from the multiple scattering (shape resonances) of the excited electron (XANES).

This paper presents the XANES and EXAFS results obtained with calcium-carbon samples containing different metal contents. The samples have been submitted to heat treatments at different temperatures under an inert atmosphere. The objective is to analyze the evolution of the local structure and the calcium dispersion in samples with calcium contents below and above the saturation of carboxylic groups on the carbon. The effect of pH during the ion-exchange process is also analyzed.

EXPERIMENTAL

Sample preparation was fully described in previous publications (1, 11). Briefly, a char from phenol-formaldehyde polymer resin (A) has been oxidized with HNO_3 (A2). Calcium has been introduced by

ion-exchanged with 1.5 M calcium acetate solution (the pH was not controlled) (A2-II-2.9) and at pH=10 (A2-II-4.1). Impregnation has been used to obtain other calcium contents. The impregnated samples were not washed. All calcium samples were dried at 383 K under vacuum. In the nomenclature II stands for ion-exchange and I for impregnation, and the calcium loading (wt %) is also included.

Samples have been treated in He at a flow rate of 60 ml/min at a heating rate of 20 K/min to reach different temperatures (603, 823 and 1223 K). Once the final temperature is reached, the sample is cooled down under the same atmosphere and sealed. Wafers for XAFS experiments were prepared under inert atmosphere pressing an homogeneous mixture of calcium-carbon sample and polyethylene in a ratio 2/1. Finally The samples were sealed with a polyethylene film to prevent air contact during handling.

The X-ray absorption experiments were performed at the Photon Factory in the National Laboratory for High Energy Physics (KEK-PF) Tsukuba (Japan). A Si (111) double crystal was used to monochromatize the X-ray from the 2.5-GeV electron storage ring, and the Ca K-edge absorption spectra were recorded in the transmission mode at room temperature in a range of photon energy extending from 3940 to 4720 eV. Special attention was paid to eliminate the photons from higher-order diffraction using double mirror system. Fourier Transformation was performed on k^2 -weighted EXAFS oscillation, $k^2\chi(k)$, in the range of 4-10 \AA^{-1} . The physical basis and numerous applications of XAFS spectroscopy have been discussed elsewhere (5,6,8).

RESULTS AND DISCUSSION

Reference compounds

Figure 1 presents XANES spectra and Fourier transformation of the EXAFS oscillations (FT-EXAFS) of several calcium compounds used as references. The most relevant aspects to consider are:

XANES spectra

- a) Calcium oxide exhibits a pre-edge peak (I) at ≈ 4043 eV.
- b) Calcium carbonate exhibits a sub-peak (II) at ≈ 4059 eV. The pre-edge peak is much less intense than in the calcium oxide.
- c) Calcium acetate exhibits only one broad main peak without any sub-peak.

The pre-edge peak evolution, which is not present in the calcium acetate spectrum, is determined by the presence of different anions in the compounds: O^{2-} , CO_3^{2-} , CH_3COO^- . Differences in ionic character and symmetry originate different modification in the valence orbital of the calcium.

Fourier transform of EXAFS oscillation

- A) Calcium oxide exhibits Ca-O peaks corresponding to distances ≈ 2.0 \AA (uncorrected for phase shift) and Ca-Ca at ≈ 3.0 \AA due to neighboring oxygen and calcium atoms respectively. Peaks appearing at higher distances correspond to Ca^{2+} and O^{2-} ions in more distant neighbor shells in the calcium oxide crystal.
- B) Calcium carbonate exhibits Ca-O peaks at ≈ 1.9 \AA and Ca-Ca at ≈ 3.7 \AA .
- C) Calcium acetate exhibits only a Ca-O peak at ≈ 2.0 \AA .

Again, anions difference is the responsible of change in local atomic arrangement from one compound

to another.

Sample A2-II-2.9

Figure 2 shows the XAFS spectra (XANES and FT-EXAFS) corresponding to sample A2-II-2.9 treated at 603 K (Figure 2a, A) and 1223 K (Figure 2b, B).

According to TPD results in Figure 3 and to the interpretation given elsewhere (1), a heat treatment at 603 K does not produce carboxylic groups decomposition which occurs around 700 K. A heat treatment at 603 K only produces H₂O and CO₂ evolution. The former coming from H₂O in the carbon itself and in the coordination sphere of calcium. The second arising from CO₂ chemisorbed on calcium ion-exchanged. This interpretation is fully confirmed by XAFS results as will shall discuss now.

XANES spectrum (Figure 2a) presents a broad main peak without any shoulder. FT-EXAFS oscillations exhibit only one Ca-O peak at ≈ 2.0 Å and no Ca-Ca peak is present. Comparing these spectra with those of reference compounds a large similarity is found with calcium acetate. This indicates that calcium is still linked to carboxylic groups at 603 K, in agreement with published results (1, 2).

The presence of a small pre-edge peak (III) in XANES spectrum (Figure 2a) indicates that coordination of oxygen atoms around calcium atom is somewhat distorted from an ideal octahedral symmetry (3, 4, 10). The evolution of H₂O and CO₂ from the coordination sphere of calcium during heat treatment at 603 K can explain this distortion.

Sample treatment at 1223 K produces important modifications in XAFS spectra. XANES spectrum (Figure 2b) shows the presence of a new pre-edge peak around 4043 eV (I) in addition to a shoulder around 4065 eV. The intensity of the pre-edge peak (III) slightly decreases in relation to that of sample treated at 603 K. FT-EXAFS spectrum (Figure 2B) presents a Ca-O peak ≈ 2.0 Å beside a very weak Ca-Ca peak, indicating that most of the calcium species are highly dispersed and/or forming amorphous small cluster with spectra characteristics similar to those of CaO (Figure 1 a, A) (3). These results are also in good agreement with previous results in which a high calcium dispersion was found when this sample was submitted to a similar heat treatment. Using CO₂ chemisorption the dispersion was 55 % (12).

Sample A2-II-4.1

This sample has been prepared by ion-exchange with a controlled pH of 10 unlike sample A2-II-2.9 which has been prepared by the same procedure but with the pH proper of the calcium acetate solution in contact with the carbon.

Figure 4 presents the TPD spectrum of sample A2-II-4.1. The most relevant aspect to be observed is the presence of a CO₂ peak at around 1050 K which does not appear in the TPD profile of sample A2-II-2.9 (Figure 3). This CO₂ peak presumably come from the CaCO₃ formed during sample preparation and not from calcium acetate, since no peak of mass 43 (characteristic of acetate) is present (1). Working at a high pH values, calcium carbonation is very probable and this will explain the above suggestion. The amount of calcium forming carbonate can be quantified from the CO₂ + 1/2 CO corresponding to this second peak. The amount obtained by this method is 0.5 wt%, therefore, the calcium ion exchanged would be 3.6 wt% which is in good agreement with the maximum calcium exchange capacity (3.5 wt%) of carbon A2 (1, 11).

XANES and FT-EXAFS spectra of sample A2-II-4.1 treated at 1223 K, appearing in Figure 5, present characteristics of CaO as in sample A2-II-2.9, but the peak intensity for the Ca-Ca peak is quite larger in the former indicating that part of the calcium is present as CaO particles with an structural order at longer range than the first coordination shell.

The disappearance of the pre-edge peak at ≈ 4040 eV indicates a smaller distortion of the calcium coordination sphere (in respect to that of sample A2-II-2.9) which again confirms the existence of a longer range order in CaO beyond the first coordination sphere. Probably, this increase in particle size from sample A2-II-2.9 to A2-II-4.1 is due to the presence of CaCO_3 formed during the sample preparation, as mentioned before.

Samples A2-I-6.0 and A2-I-9.4

Calcium content in these samples is larger than the maximum ion-exchange capacity of the carbon (3.5 wt%). According to the interpretation previously mentioned (1, 11), calcium in excess appears as calcium acetate crystals over the ion-exchanged one. These conclusions arise from the TPD study on these samples as well as from TG-DTA and XRD (11). TPD spectra present a peak of mass 43 at around 730 K coming from the calcium acetate decomposition and peaks of CO_2 and CO at ≈ 1030 K produced in the CaCO_3 decomposition (1).

To distinguish between different steps in calcium acetate decomposition, samples have been treated at different temperatures before XANES and FT-EXAFS spectra were recorded. Sample A2-I-6.0 has been treated at 823 and 1223 K, the results appear in Figure 6. Sample A2-I-9.4 has been treated at 603, 823 and 1223 K and the spectra are shown in Figure 7.

Heat treatment up to 603 K produces CO_2 and H_2O evolution from: a) the carbon (adsorbed H_2O), b) the calcium acetate (H_2O of crystallization) and c) the ion-exchanged calcium (CO_2 and H_2O coordinated). Calcium acetate remain unchanged.

From XANES and FT-EXAFS spectra similar conclusions are obtained. Figure 7 a, A shows the presence of only one broad peak in XANES spectrum and a quite intense Ca-O peak in FT-EXAFS similar to those of calcium acetate. Furthermore, the pre-edge peak (III) at ≈ 4040 eV is smaller than that for sample A2-II-2.9 treated at the same temperature (Figure 2 a, A) indicating a higher order at longer distance.

Spectra obtained after a treatment at 823 K exhibits characteristics of CaCO_3 in agreement with previous results (1, 11). It is interesting to observe the decrease of the pre-edge peak (at ≈ 4030 eV) from the spectrum of sample A2-I-6.0 to that of A2-I-9.4 which is indicative of a higher order at longer distance presents in CaCO_3 particle for the second sample. This observation is confirmed with the fact that Ca-Ca peak intensity is much higher for sample A2-I-9.4 than A2-I-6.0.

Finally, a heat treatment at 1223 K produces CaCO_3 decomposition to yield CaO (1, 11). This is also observed in Figures 6 b, B and 7 c, C. The spectra exhibit clearly the CaO characteristics. By comparison of FT-EXAFS results of samples heat treated up to 1223 K as a function of calcium content it is clear that as the calcium content increases the spectra look more similar to those of bulk calcium oxide. Therefore the CaO particle size increase in agreement with previous results (1, 11). Calcium dispersion was found to decrease from 0.55 (sample A2-II-2.9) to 0.35 (sample A2-I-9.4).

CONCLUSIONS

Sample with calcium content below the ion-exchange capacity of the carbon has, after heat treatment, most of the calcium species highly dispersed forming amorphous small cluster of CaO. Increasing pH, during ion-exchange, the calcium loading increases, however, a partial carbonation occurs leading to a particle size increase after heat treatment.

XANES and FT-EXAFS results in samples heat treated up to 1223 K clearly show that as calcium content increases the spectra look more similar to those of bulk calcium oxide indicating an increase in CaO particle size.

XANES and FT-EXAFS study fully confirms previous conclusions obtained in the TPD study carried out in these samples.

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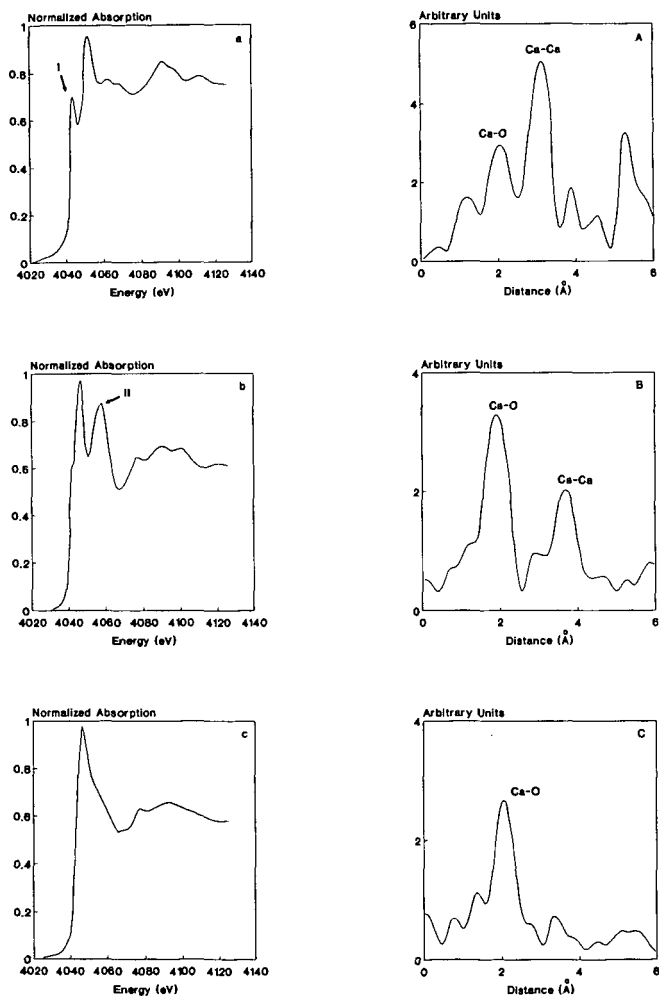


Figure 1. XANES spectra (a, b, c) and FT-EXAFS (A, B, C) of reference compounds: a, A) calcium oxide; b, B) calcium carbonate and c, C) calcium acetate.

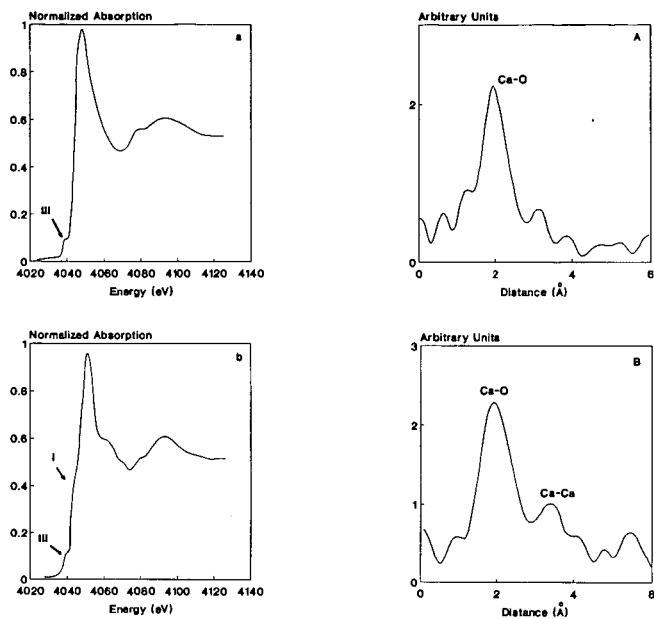


Figure 2. XANES spectra (a, b) and FT-EXAFS (A, B) of sample A2-II-2.9 after heat treatment at: a, A) 603K and b, B) 1223K.

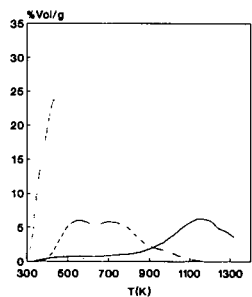


Figure 3. TPD spectrum of sample A2-II-2.9 (---, H₂O; —, CO; -·-, CO₂).

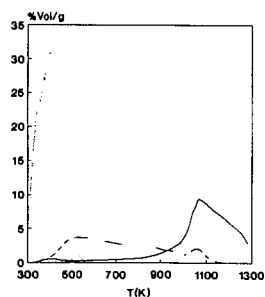


Figure 4. TPD spectrum of sample A2-II-4.1 (---, H₂O; —, CO; -·-, CO₂).

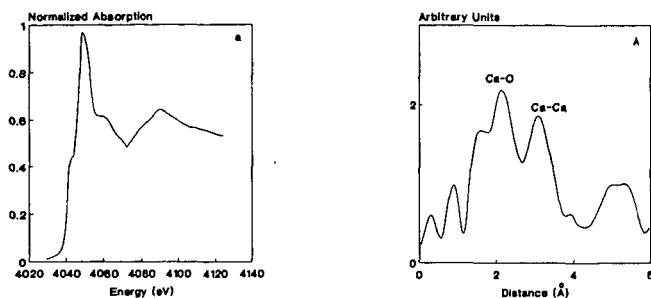


Figure 5. XANES spectra and FT-EXAFS of sample A2-II-4.1 after heat treatment at 1223 K.

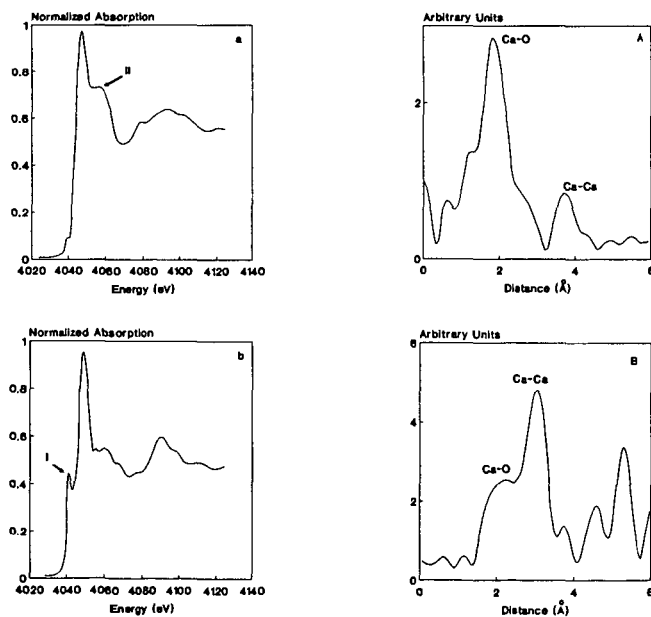


Figure 6. XANES spectra (a, b) and FT-EXAFS (A, B) of sample A2-I-6.0 after heat treatment at: a, A) 823 K and b, B) 1223 K.

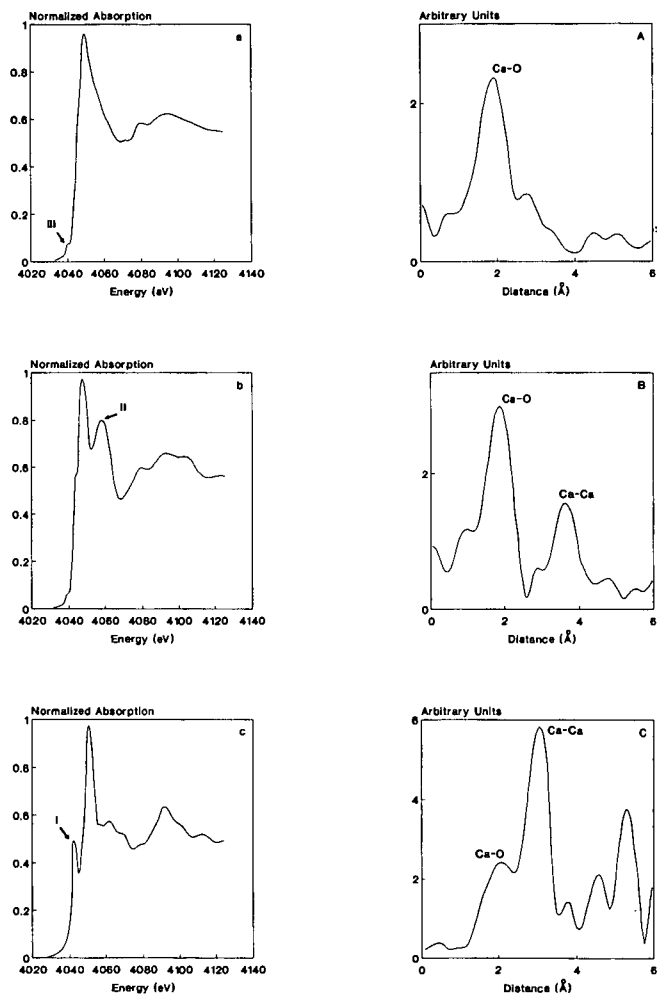


Figure 7. XANES spectra (a, b, c) and FT-EXAFS (A, B, C) of sample A2-I-9.4 after heat treatment at: a, A) 603 K; b, B) 823 K and c, C) 1223 K.